**PCT** WORLD PATENT ORGANIZATION
International Office
INTERNATIONAL PATENT APPLICATION PUBLISHED IN ACCORDANCE WITH THE TREATY ON INTERNATIONAL COOPERATION IN THE AREA OF PATENTS (PCT)

| 51 International Patent Classification: **A61K 7/06** | **A1** | 11 International Publication No.: **WO 97/23193**<br>43 International Publication Date: July 3, 1997(07/03/1997) |
|---|---|---|

21 International File No.: PCT/FR96/01831

22 International Application Date: November 19 1996 (11/19/1996)

30 Data related to priority:
95/15290 December 21 1995 (12/21/1995) FR

71 Applicant *(for all contracting states except US)*:
L'OREAL (FR/FR); 14, rue Royale, F-75008 Paris (FR)

72 Inventors; and
75 Inventors/Applicants *(US only)*: CAUWET-MARTIN, Daniele (FR/FR); 53 rue de Charonne, F-75011 Paris (FR); LION, Bertrand, (FR/FR); 2, rue Denis-Papin, F-93190 Livry-Gargan (FR); MONDET, Jean (FR/FR); 90, rue Roger-Lemaire, F-93600 Aulnay-sous-Bois (FR).

74 Representative: MISZPUTEN, Laurent; L'Oreal - D.P.I., 90, rue du General-Roguet, F-92583 Clichy Cedex (FR).

81 Contracting states: AL, AM, AU, AZ, BB, BG, BR, BY, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, RG).

Published
*With International Search Report*

54 Title: COMPOSITIONS FOR THE TREATMENT OF KERATINIC MATERIALS CONTAINING THE ASSOCIATION OF A POLYAMPHOLYTE POLYMER AND A CATIONIC POLYMER

57 Abstract

The invention relates to a composition for the treatment of keratinic materials, particularly human hair, containing in a cosmetically and/or dermatologically acceptable aqueous medium at least: a) a polyampholyte polymer comprised of at least one ethylenically unsaturated monomer and comprising in the chain or sideways of the chain equimolar or substantially equimolar quantities of negative charges and positive charges; said polymer is water insoluble at a concentration higher than or equal to 1% by weight at 20°C; b) a cationic polymer of which the cationic charge density is lower than or equal to 4 meq/g. They are to be used as hair products to be rinsed off for washing, care and/or styling. They have a good styling effect and good properties for the disentangling of wet hair.

# COMPOSITIONS FOR THE TREATMENT OF KERATINIC MATERIALS CONTAINING A COMBINATION OF A POLYAMPHOLYTE POLYMER AND A CATIONIC POLYMER

The present invention relates to new compositions for the treatment of keratinic materials, in particular hair, containing a combination of a polyampholyte polymer and a cationic polymer, as well as their uses.

For several years, in the field of shampoos and after-shampoos, conditioning products for the hair have been sought that permit the imparting of additional cosmetic effects after application and rinsing. In particular, it has been sought to produce shampoos and after-shampoos that impart styling properties.

In the patent application JP 7-15115 and the US patent 4,994,088 shampoo compositions based on polyampholyte polymers are considered. These are special polyelectrolyte polymers having equimolar (or essentially equimolar) quantities of negative charges and positive charges. These polymers are generally insoluble in water and have the characteristic of being deposited on the hair by dilution and precipitation during the rinsing step and of fixing and/or maintaining the hair after application of the shampoo.

The polyampholyte polymers, however, present the disadvantage of impeding the disentangling of the wet hair.

The applicant has discovered that by combining these polyampholyte polymers with certain cationic polymers that will be defined below, it is possible to obtain, surprisingly, rinsed hair products that, after application, bring both styling properties and good disentangling properties for damp hair.

The compositions according to the invention are essentially characterized by the fact that they contain in a cosmetically and/or dermatologically acceptable medium at least:

a) a polyampholyte polymer constituted of at least one ethylenically unsaturated monomer containing in the chain or laterally to the chain equimolar or practically equimolar quantities of negative charges and positive charges, the said polymer being insoluble in water at a concentration higher than or equal to 1% by weight at 20°C;

b) a cationic polymer in which the cationic charge density is less than or equal to 4 meq/g.

The "polyampholyte" polymers corresponding to the definition indicated above, in accordance with the invention have a global charge of approximately zero and a pH of approximately 7.

These polymers are in general insoluble in water at a concentration higher than or equal to 0.1% by weight at 20°C. Some of them can be solubilized in aqueous solutions of electrolytes, preferably containing inorganic electrolytes. Some can likewise be solubilized directly in a detergent base based on surfactants, others are solubilized in a detergent base in the added presence of electrolytes. The solubility of these polymers in aqueous mediums will depend on the structure of the polyampholyte chosen. In general, these polymers are going to be able to be deposited on to the hair by dilution and precipitation during the rinsing, whether or not they are applied in the presence of electrolytes and/or surfactants.

The polyampholyte polymers of the present invention are preferably chosen from the group constituted by:

(1) Polymers of the following formula:

$$-\underset{D^{(-)},\,X^{(+)}}{\underset{|}{(A-)}}{}_{x_1}-(B-)_y-\underset{E^{(+)},\,Y^{(-)}}{\underset{|}{(C-)}}{}_{x_2}- \qquad \text{(I)}$$

in which:

A designates a group resulting from the copolymerization of an ethylenically unsaturated monomer bearing a group $D^{(-)}$

$D^{(-)}$ designates an anionic group chosen from the group constituted by:

(i) $-COO^{\ominus}$

(ii) $-SO_3^{\ominus}$

(iii) $-PO_3^{2\ominus}$

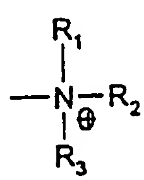
(iv) $-HPO_3^{\ominus}$

$X^{(+)}$ designates a cation arising from the neutralization of the D groups by an inorganic or organic base;

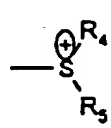
B is a group resulting from the copolymerization of at least one ethylenically unsaturated hydrophobic or hydrophilic monomer, preferably of low polarity;

C is a group resulting from the copolymerization of an ethylenically unsaturated monomer bearing a group $E^{(+)}$;

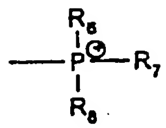
$E^{(+)}$ designates a cationic group chosen from the group constituted by:

(i) 

in which $R_1$, $R_2$ and $R_3$, which are identical or different, designate hydrogen, a linear, branched or cyclic (cycloaliphatic or aromatic) $C_1$-$C_{22}$ alkyl group;

(ii) 

in which $R_4$ and $R_5$, which are identical or different, designate an aliphatic, cycloaliphatic or aromatic group;

(iii) 

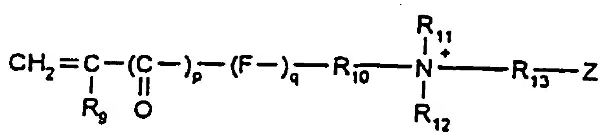
where $R_6$, $R_7$, and $R_8$, which are identical or different, designate an aliphatic, cycloaliphatic or aromatic group.

$Y^{(-)}$ designates an anion resulting from the neutralization of the E groups by an inorganic or organic acid or the quaternization of the E groups;

$x_1$, $x_2$ and y respectively designate the molar percentages in group A, in group B and in group C,

$x_1$ and $x_2$ being identical or essentially identical so that the global charge of the polymer is approximately 0 for a pH close to 7, the sum $x_1 + x_2$ preferably being higher than or equal to 40 mole % and preferably being lower than or equal to 60 mole %.

(2) betaine polymers of the following formula:

 (II)

in which:

$R_9$, $R_{11}$ and $R_{12}$, which are identical or different, designate hydrogen or a linear or branched $C_1$-$C_4$ alkyl;

Z designates $COO^{(-)}$, $SO_3^{(-)}$ or $HPO_3^{(-)}$;

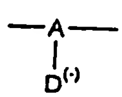
F designates NH or O or with the group $R_{10}$ forms an aromatic or non-aromatic $C_5$-$C_7$ ring or heterocycle;

$R_{10}$ and $R_{13}$, independently of each other, designate a divalent hydrocarbon group, in particular a $-(CH_2)_n-$ group with n being a whole number between 1 and 4;

$R_{10}$ with $R_{11}$ and $R_{12}$ can form a $C_5$-$C_7$ heterocycle;

p is 0 or 1 and q is 0 or 1.

In the general formula (I) as defined above, the monomers lead, after copolymerization, to units of structure:



When $D^{(-)}$ designates a carboxylate function, these monomers are chosen from among the salts of linear, branched or cyclic (cycloaliphatic or aromatic) carboxylic acids such as the salts of crotonic acid, acrylic acid, methacrylic acid, vinylbenzoic acid; the salts of carboxylic diacids such as the salts of maleic, fumaric, or itaconic acid as well as their monoesters and monoamides;

when $D^{(-)}$ designates the sulfonate function, the monomers are chosen from among the salts of 2-acrylamido-2-methylpropane sulfonic acid, of vinylsulfonic acid and of styrenesulfonic acid in the neutralized form; salts of 2-sulfoethyl (meth)acrylate;

when $D^{(-)}$ designates the phosphonate function, the monomers are for example the salts of neutralized vinylphosphonic acid.

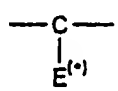
The counter ion $X^{(+)}$ associated with $D^{(-)}$ results in general from the neutralization of a D group by an inorganic base such as NaOH or KOH or an organic base such as an amine or aminoalcohol.

In the general formula (I), the monomers leading to units of structure -B- are chosen from among the hydrophilic or hydrophobic ethylenically unsaturated monomers, more particularly of low polarity, and are chosen in such a way that the final polymer is not soluble in water in the absence of an electrolyte and/or surfactant.

As examples may be cited the vinyl monomers such as the linear branched or cyclic $C_1$-$C_{24}$ vinyl esters, olefins such as ethylene, styrene and its substituted derivatives; the linear, branched or cyclic $C_1$-$C_{24}$ esters or amides of (meth)acrylic acid.

The monomers leading by copolymerization to -B- units can be polymerized with silicone macromers having a terminal vinyl function. They can also be copolymerized by monomers with fluoro or perfluoro groups of the vinyl, allylic or (meth)acrylic type such as for example vinylidene fluoride, chlorotrifluoroethylene, tetrafluoroethylene; the perfluoro (meth)acrylates such as perfluorohexyl or perfluorooctyl (meth)acrylate.

In the general formula (I), the monomers leading, after copolymerization, to units of structure -C- are preferably



chosen from among monomers of the (meth)acrylic, vinyl, allylic or diallylic type containing a tertiary amine function quaternized by an alkyl halide or a dialkyl sulfate.

Examples that may be cited are:

- dimethylaminoethyl(meth)acrylate,
- diethylaminoethyl(meth)acrylate,
- dimethylaminopropyl(meth)acrylate,
- dimethylaminopropyl(meth)acrylamide,
- 2-vinylpyridine,
- 4-vinylpyridine,
- dimethylallylamine,

quaternized by an alkyl halide or a dialkyl sulfate.

The particularly preferred polyampholytes of formula (I) are chosen from among the sodium styrene sulfonate/trimethylammonio ethylmethacrylate chloride copolymers and the styrene sulfonate* /trimethylammonio propyl-(meth)acrylamide chloride copolymers.

*[* Translator's note: this should read <u>sodium</u> styrene sulfonate - see Preparation Example 2 on p. 17 of original; see also Claim 9]*

The molecular weights of the polyampholytes can vary from 500 to 50,000,000 and are preferably higher than 10,000.

The particularly preferred polyampholytes of formula (II) are chosen from the group constituted by:

poly 1-vinyl-2-(3-sulfopropyl) imidazolium hydroxide (J.C. Salamone, Polymer vol. 19, p. 1157, 1978);
poly 1-vinyl-3-(3-sulfopropyl) imidazolium hydroxide;
poly 1-vinyl-3-(4-sulfobutyl) imidazolium hydroxide;
poly 1-vinyl-2-methyl-3-(4-sulfopropyl) imidazolium hydroxide;
poly 2-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly 2-methyl-5-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly 4-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly dimethyl-(2-methacryloxyethyl)-3-sulfopropyl) ammonium hydroxide;
poly diethyl-(2-methacryloxyethoxy-2-ethyl)-(3-sulfopropyl) ammonium hydroxide;
poly 4-vinyl-4-(sulfobutyl) pyridinium hydroxide;
poly N-(3-sulfopropyl)-N-methacrylamidopropyl-N,N-dimethylammonium betaine

These polysulfobetaines are listed in the Encyclopedia of Polymer Science and Engineering, 2nd edition, vol. 11, p. 517.

The polyampholytes of formula (I) can be synthesized by direct copolymerization in solution in water with or without electrolyte, or by polymerization in solution in a water/organic solvent medium. They can be obtained by copolymerization by precipitation or polymerization in dispersion in a water/organic solvent medium.

The general methods of polymerization of these polymers are described in the Encyclopedia of Polymer Science and Engineering, 2nd edition, vol. 11, p. 521, Wiley Interscience.

They can also be obtained by reverse emulsion polymerization in the presence of water and an organic solvent in accordance with the procedure described in the article by J.M. Corpart and F. Candau, Macromolecules, vol. 26, No. 6, p. 1333, 1993.

They can also be obtained by "micellar" copolymerization in water by a procedure described in the article by I. Lacik, Polymer 36(16), 3197-3211, 1995.

When the polymerization is carried out in solution in water, a water-soluble primer such as sodium or potassium persulfate or a redox system is used.

When the polymerization is effectuated in organic or aqueous organic medium, organic primers can also be used. To control the final molecular weight, the presence of a transfer agent in the polymerization medium may be necessary.

The monomers constituting the invention polyampholytes are preferably already neutralized and/or quaternized. When working with already-neutralized monomers in solution in water, during the polymerization a mutual self-neutralization of the anionic and cationic groups is observed, which can cause the precipitation of the polymer formed.

When working in a medium diluted in water, during the polymerization a total or partial expulsion of the counter ions $X^+$ and $Y^-$ into the aqueous solution is observed.

The polyampholytes of formula (I) can also be obtained by direct polymerization of the pair of monomer ions:

$$\begin{array}{c} A \\ | \\ D^{(-)} \end{array} \qquad \begin{array}{c} \text{et} \\ \text{and} \end{array} \qquad \begin{array}{c} C \\ | \\ E^{(+)} \end{array}$$

in accordance with the method described by J.C. Salamone in the article extracted from J. Macromol. Sc. Chem. A22 (5-7), pp. 653-664 (1985).

The polyampholyte polymers of formula (II) can be obtained by synthesis of the already betainized monomer by effectuating a quaternization reaction then polymerization. They can also be obtained by making the polymer with amino groups then quaternizing.

The invention polyampholyte polymers are present in the invention compositions in proportions of preferably from 0.01 to 20% by weight and more particularly from 0.1 to 10% by weight relative to the total weight of the composition.

The cationic polymers used in accordance with the invention generally have an average molecular weight of at least 5000, preferably at least 10,000 and less than 10,000,000, and more particularly of from 100,000 to 2,000,000. In general, they have units containing a nitrogen atom such as quaternary ammonium or amino units or their mixtures. Their cationic charge density is lower than or equal to 4 meq/g, preferably higher than or equal to 0.9 meq/g, and more preferably between 1.1 and 3 meq/g. The charge density can be determined by the Kjeldahl method. In general, it corresponds to a pH of the order of 3 to 9.

Among the cationic polymers that can be used in accordance with the invention may be cited the copolymers of vinyl monomers having amine or quaternary ammonium functions and water-soluble ethylenically unsaturated monomers such as acrylamide, methacrylamide, alkyl or dialkyl (meth)acrylamides, alkyl (meth)acrylates, vinyl caprolactone, vinyl pyrrolidone, or many other monomers such as the vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol, ethylene glycol. The alkyl or dialkyl groups of the amine or ammonium functions are preferably $C_1$-$C_9$ and more preferably $C_1$-$C_3$.

The amines can be primary, secondary or tertiary. The secondary and tertiary amines are preferred.

The amino-substituted vinyl monomers can be polymerized in their amine form then eventually quaternized. The amines can also be quaternized after the formation of the polymer. For example, tertiary amine functions can be quaternized by reaction with a salt of formula R'X where R' is a short-chain alkyl radical (preferably $C_1$-$C_7$ and more particularly $C_1$-$C_3$) and X is an anion forming a water-soluble salt with the quaternary ammonium.

Among the vinyl monomers with amine or quaternary ammonium functions may be cited for example vinyl compounds substituted by a group of the dialkylaminoalkyl (meth)acrylate and monoalkyl-

aminoalkyl (meth)acrylate type; salts of trialkyl-methacryloxyalkyl ammonium; diallyl quaternary ammonium salts; quaternary vinyl monomers having rings bearing quaternized nitrogen atoms such as pyridinium, imidazolium, quaternized pyrrolidone such as alkylvinylimidazolium, alkylvinylpyridinium, quaternary salts of alkylvinylpyrrolidone. The alkyl portions of these monomers are preferably $C_1$-$C_3$ alkyls and more preferably $C_1$ or $C_2$ alkyls.

Also to be cited as amino-substituted vinyl monomers are the dialkylaminoalkyl (meth)acrylates and the dialkylaminoalkyl (meth)acrylamides. The alkyl or dialkyl groups are preferably $C_1$-$C_9$ and more preferably $C_1$-$C_3$ alkyls.

The cationic monomers of the invention can include mixtures of vinyl monomers derived from amines and/or vinyl monomers derived from quaternary ammoniums and/or other compatible monomers. As examples may be cited:

- the copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (for example chloride) (called Polyquaternium-16 by the CTFA), such as those sold under the name LUVIQUAT by the BASF company;

- the copolymers of 1-vinylpyrrolidone and dimethylaminoethylmethacrylate (called Polyquaternium-11 according to the CTFA), such as those sold under the name GAFQUAT (for example GAFQUAT 755N) by the GAF Corporation;

- the homopolymers of dimethyl-diallylammonium chloride (Polyquaternium-5 according to the CTFA) and the copolymers of acrylamide and dimethyldiallylammonium chloride (Polyquaternium-7 according to the CTFA), such as those sold under the name MERQUAT 550 and MERQUAT S by the MERCK company;

- the inorganic acid salts of aminoalkyl esters of homo and copolymers of unsaturated carboxylic acids having 3 to 5 carbon atoms, such as those described in the US patent 4,009,256.

Among the cationic polymers that can be used may also be cited the cationic polysaccharides, such as cationic derivatives of cellulose and cationic derivatives of starch.

Among the cationic polysaccharides may be cited the polymers of formula:

$$\mathrm{H{-}O{-}(-R{-}}\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\overset{|}{\underset{|}{N^+}}}}\mathrm{{-}R^3G^-)}$$

where:

H is an anhydroglucose residue such as starch or a cellulosic residue of anhydroglucose;

R is an alkylene, oxyalkylene, polyoxyalkylene or hydroxyalkylene or their mixtures;

$R^1$, $R^2$ and $R^3$, which are identical or different, designate an alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl group, each group containing up to 18 carbon atoms, and the total number of carbon atoms per cationic unit being preferably less than or equal to 20;

$G^-$ is an anion resulting from the quaternization of the amine $NR^1R^2R^3$.

Among the cationic cellulosic polymers may be cited those sold by the AMERCHOL Corp. under the names JR and LR, such as the quaternary salts of hydroxyethylcellulose obtained by reaction with an epoxide substituted by a trimethylammonium (Polyquaternium-10 according to the CTFA). Also to be cited are the quaternary salts of hydroxyethylcellulose obtained by reaction with an epoxide substituted by lauryl-dimethylammonium (Polyquaternium-24 according to the CTFA), such as those sold under the name POLYMER LM200 by AMERCHOL Corp.

Also cited as cationic polymers that can be used in accordance with the invention are the cationic derivatives of guar gum, such as the chloride of guar hydroxypropyltrimonium sold under the JAGUAR names by CELANESE Corp.

Also to be cited are the quaternary cellulose ethers such as those described in the US patent 3,962,418 and the etherified copolymers of cellulose and starch such as those described in the US patent 3,958,581.

The cationic polymers of the invention are present in the compositions in proportions of, preferably, from 0.01 to 5% by weight and more preferably from 0.1 to 3% by weight relative to the total weight of the composition.

The aqueous compositions of the invention can contain in addition inorganic or organic electrolytes permitting the solubilization of the polyampholyte polymers.

The electrolytes used are preferably water-soluble inorganic salts such as the salts of alkali metals, salts of alkaline earth metals, or the aluminum salts of hydrochloric, sulfuric or nitric acid or of an organic acid such as citric, lactic or tartaric acid. The electrolytes particularly preferred are chosen from among potassium sulfate, sodium sulfate, magnesium sulfate, calcium nitrate, aluminum nitrate, magnesium nitrate, sodium chloride, potassium chloride, aluminum chloride, potassium carbonate, sodium carbonate, aluminum carbonate, and sodium citrate.

They are present in proportions of from 0.1 to 30% by weight, and more preferably from 1 to 10% by weight relative to the total weight of the composition.

The pH of the aqueous solutions according to the invention is preferably adjusted to between 3 and 11, and more particularly between 5 and 9 by the use of alkalinizing or acidifying agents or of buffers. It is important to adjust the pH in such a way that the polyampholyte polymer in dissolved or dispersed form in the aqueous medium of the composition can precipitate by dilution during the rinsing step after application of the composition on to keratinic materials.

The compositions according to the invention, when they are presented in particular in the form of a shampoo, include a detergent base, generally aqueous. This surfactant base can also serve to solubilize the polyampholyte or polyampholytes in the aqueous medium.

The surfactant or surfactants forming the detergent base can be chosen indiscriminately, alone or in mixtures, from among the anionic, amphoteric, non-ionic, zwitterionic and cationic surfactants.

The minimum quantity of detergent base is that just sufficient to endow the final composition with a satisfactory foaming and/or detergent power and/or to solubilize the polyampholytes present in the composition.

Thus, according to the invention, the detergent base can represent 4% to 30% by weight, preferably 10% to 25% by weight, and still more preferably 12% to 20% by weight of the total weight of the final composition.

The surfactants that are suitable for the effectuation of the present invention are in particular the following:

(i) Anionic surfactant(s):

Their nature, within the framework of the present invention, is not particularly critical.

Thus, as an example of anionic surfactants that can be used alone or in a mixture, within the framework of the present invention, may be cited in particular (non-limiting list) the salts (particularly alkaline salts, especially of sodium, ammonium salts, amine salts, aminoalcohol salts or magnesium salts) of the following compounds: alkyl sulfates, alkylether sulfates, alkylamidoether sulfates, alkylarylpolyether sulfates, monoglyceride sulfates; alkyl sulfonates, alkyl phosphates, alkylamide sulfonates, alkylaryl sulfonates, α-olefin sulfonates, paraffin sulfonates; alkylsulfosuccinates, alkylethersulfosuccinates, alkylamide sulfosuccinates; alkyl sulfosuccinamates; alkylsulfoacetates; alkylether phosphates; acyl sarcosinates; acylisethionates and N-acyltaurates, the alkyl or acyl radical of all these different compounds preferably including 12 to 20 carbon atoms, and the aryl radical preferably designating a phenyl or benzyl group. Among the anionic surfactants that can also be used may also be cited the salts of fatty acids such as the salts of oleic, ricinoleic, palmitic, stearic acids, acids of copra oil or hydrogenated copra oil; acyl-lactates in which the acyl radical contains 8 to 20 carbon atoms. Also used can be the weakly anionic surfactants, such as the uronic acids of alkyl D-galactoside and their salts, as well as the polyoxyalkylenated carboxylic acid ethers, in particular those containing 2 to 50 ethylene oxide groups, and their mixtures. The anionic surfactants of the polyoxyalkylenated carboxylic ether acid or salt type are in particular those corresponding to the following formula (1):

$$R_1\text{—}(\text{-}OC_2H_4\text{-})_n\text{—}OCH_2COOA \qquad (1)$$

in which:

$R_1$ designates an alkyl or alkylaryl group, and n is a whole or decimal number (average value) that can vary between 2 and 24, preferably from 3 to 10, the alkyl radical having between about 6 and 20 carbon atoms, and aryl preferably designating phenyl,

A designates H, ammonium, Na, K, Li, Mg, or a monoethanolamine or triethanolamine residue. Mixtures of compounds of formula (1) may also be used, particularly mixtures in which the $R_1$ groups are different.

Compounds of formula (1) are sold for example by the CHEM Y company under the AKYPOS names (NP40, NP70, OP40, OP80, RLM25, RLM38,RLMQ38 NV, RLM 45 RLM 45 NV, RLM 100, RLM 100 NV, RO20, RO 90, RCS 60, RS 60, RS 100, RO 50) or by the SANDOZ company under the SANDOPAN names (DTC Acid, DTC).

(ii) Non-ionic surfactant(s):

The non-ionic surfactants are also well-known compounds (see in particular in this regard "Handbook of Surfactants" by M.R. Porter, Blackie and Son Editions (Glasgow and London), 1991, pp. 116-178) and their nature is not particularly critical in the framework of the present invention. Thus they can in particular be chosen from among (non-limiting list) the alcohols, alpha-diols, alkylphenols or polyethoxylated, polypropoxylated or polyglycerolated fatty acids having an aliphatic chain containing for example 8 to 18 carbon atoms, the number of ethylene oxide groups or propylene oxide groups

being in particular from 2 to 50 and the number of glycerol groups being in particular from 2 to 30. Also cited may be the copolymers of ethylene oxide and propylene oxide, condensates of ethylene oxide and propylene oxide on fatty alcohols; polyethoxylated fatty amides preferably having 2 to 30 moles ethylene oxide, polyglycerolated fatty amines containing on the average 1 to 5 glycerol groups and in particular 1.5 to 4; polyethoxylated fatty amines preferably having 2 to 30 moles ethylene oxide; oxyethylenated sorbitan esters of fatty acids having 2 to 30 moles ethylene oxide; sucrose esters of fatty acids, polyethylene glycol esters of fatty acids, alkylpolyglycosides, derivatives of N-alkylglucamine, amine oxides such as oxides of ($C_{10}$-$C_{14}$)-alkyl amines or oxides of N-acylaminopropylmorpholine. It will be noted that the alkyl polyglycosides constitute non-ionic surfactants that enter particularly well into the scope of the present invention.

(iii) Amphoteric or zwitterionic surfactant(s):

The amphoteric or zwitterionic surfactants, the nature of which is not particularly critical in the framework of the present invention, can be in particular (non-limiting list) aliphatic derivatives of secondary or tertiary amines, in which the aliphatic radical is a linear or branched chain containing 8 to 18 carbon atoms and containing at least one hydrosolubilizing anionic group (for example carboxylate, sulfonate, sulfate, phosphate or phosphonate); also cited may be the ($C_8$-$C_{20}$)-alkyl betaines, sulfobetaines, ($C_8$-$C_{20}$)-alkylamido-($C_1$-$C_6$)-alkyl betaines or the ($C_8$-$C_{20}$)-alkylamido-($C_1$-$C_6$)-alkyl sulfobetaines.

Among the amine derivatives may be cited the products sold under the name MIRANOL, such as described in the US patents 2,528,378 and 2,781,354 and classified in the CTFA dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinates and Amphocarboxypropionates of the respective structures:

$$R_2\text{-CONHCH}_2\text{CH}_2\text{-N}(R_3)(R_4)(\text{CH}_2\text{COO-}) \qquad (2)$$

in which:

$R_2$ designates an alkyl radical of an acid $R_2$-COOH present in hydrolyzed copra oil, or a heptyl, nonyl or undecyl radical,
$R_3$ designates a beta-hydroxyethyl group, and
$R_4$ a carboxymethyl group;

and

$$R_2\text{-CONHCH}_2\text{CH}_2\text{-N(B)(C)} \qquad (3)$$

in which:

B represents $-CH_2CH_2OX'$,
C represents $-(CH_2)_z-Y'$, with z = 1 or 2,
X' designates the $-CH_2CH_2COOH$ group or a hydrogen atom,
Y' designates -COOH or the $-CH_2$-CHOH-$SO_3H$ radical
$R_{2'}$ designates an alkyl radical of an acid $R_9$-COOH present in copra oil or in hydrolyzed linseed oil, an alkyl radical, in particular a $C_7$, $C_9$, $C_{11}$ or $C_{13}$ radical, a $C_{17}$-alkyl radical and its iso form, an unsaturated $C_{17}$ radical.

As an example may be cited the cocoamphocarboxyl glycinate sold under the trade name concentrated MIRANOL $C_2M$ by the MIRANOL company.

(iv) Cationic surfactants:

Among the cationic surfactants, the nature of which is not critical within the framework of the present invention, may be cited in particular (non-limiting list): salts of primary, secondary or tertiary fatty amines, possibly polyoxyalkylenated; quaternary ammonium salts such as tetraalkylammonium, alkylamido alkyltrialkylammonium, trialkylbenzylammonium, trialkylhydroxyalkylammonium or alkylpyridinium chlorides or bromides; imidazoline derivatives; or amine oxides with cationic character.

It will be noted that the cationic surfactants, the use of which is not excluded, do not constitute preferred surfactants for the effectuation of the present invention.

The cosmetically or pharmaceutically acceptable medium of the invention compositions is preferably water or an aqueous-alcoholic solution of a lower alcohol such as ethanol, isopropanol or butanol.

The compositions according to the invention can of course contain in additions the adjuvants usual in the field of compositions for the hair, such as for example perfumes, preservatives, sequestrants, thickeners, conditioners, foam modifiers, colorants, pearlizing agents, hydrating agents, anti-dandruff or anti-seborrheic agents, vitamins, sun screens and others.

Of course, one skilled in the art will be careful to choose this or these possible additional compounds and/or their quantities in such a way that the intrinsic advantages of the composition in accordance with the invention are not, or essentially not changed by the additive or additives considered.

These compositions can be presented in the form of more or less thickened liquids, creams or gels, and they are mainly suitable for washing, caring for or styling the hair. They can also be presented in the form of lotions to be rinsed off.

Another objective of the invention is a procedure for non-therapeutic treatment of the hair characterized by the fact that a composition as defined above is applied directly to the wet hair and after a possible interval a rinsing with water is carried out, this procedure being capable of being repeated several times.

As indicated previously, the compositions according to the invention impart to the hair, after rinsing, a remarkable styling effect which is manifested in particular by ease of styling and maintenance as well as a perceptibly improved disentangling of wet hair.

The examples that follow serve to illustrate the present invention without in any way being limiting in nature.

## EXAMPLES

### PREPARATION EXAMPLE 1

*Synthesis of the copolymer of sodium styrene sulfonate and trimethylammonio ethylmethacrylate chloride (50/50 mole%) of formula (I).*

Into a reactor with central mechanical stirring, cooler, thermometer and nitrogen bubbler are introduced 49.8 g powdered sodium styrene sulfonate. Then 63.63 g of a 78.9% aqueous solution of dry extract of trimethylammonio ethylmethacrylate chloride is introduced, followed by 300 g purified water plus 2 g potassium persulfate (polymerization primer). All these additions are made at ambient temperature.

The reaction mixture is stirred at 400 rpm to obtain dissolution and homogenization.

Nitrogen is bubbled in. The medium is heated to 72°C and kept at this temperature with stirring for 24 hours.

At the end of polymerization, the reaction medium is brought to ambient temperature. The medium is cloudy, but the polymer does not precipitate.

The polymer is purified by precipitation of the synthesis solution in 5 l purified water. The precipitate is recovered and dried to constant weight in a furnace at 45°C.

The elemental analysis corresponds to that of the theoretical polymer. The yield is 85%. The polymer thus obtained is insoluble in water at 1% by weight.

It can be solubilized in water at a concentration of 1% by adding a minimal amount of 3.85% by weight of NaCl. It can also be solubilized in a detergent base consisting of:

| | | |
|---|---|---|
| sodium lauryl ether sulfate | | 15% by weight |
| cocoylbetaine | | 3% by weight |
| water | qsp | 100% by weight |

at the concentration of 1% by weight by addition of a minimal quantity of 2% NaCl.

<u>PREPARATION EXAMPLE 2</u>

*Synthesis of the copolymer of sodium styrene sulfonate and trimethylammonio propylmethacrylamide chloride (50/50 mole %).*

The same conditions as those in Example 1 are used, with 48.3 g sodium styrene sulfonate, 98.48 of a 52.5% aqueous solution of dry extract of trimethylammonio propylmethacrylamide chloride, 500 g purified water and 2 g ammonium persulfate.

The elemental analysis corresponds to that of the theoretical polymer. The yield is 91%.

The polymer thus obtained is insoluble at a concentration of 1% by weight in water. It can be solubilized in water at this same concentration in the presence of at least 5.66% by weight of NaCl.

It can also be solubilized in the detergent base in Example 1 at this same concentration in the presence of at least 4.76% by weight of NaCl.

PREPARATION EXAMPLE 3

*Synthesis of the copolymer of acrylamido-2-methyl-2-propane sulfonic acid and trimethylammonio ethylmethacrylate chloride (50/50 mole%).*

The same reactor as that in Example 1 is used, with 47.42 g acrylamido-2-methyl-2-propane sulfonic acid, and 60.25 g of a 78.9% aqueous solution of dry extract of trimethylammonio ethylmethacrylate chloride.

Before the introduction of the quaternary monomer, the sulfonic monomer is introduced into the reactor, then 200 g purified water for dissolution and homogenization [is added] at ambient temperature.

The sulfonic monomer is neutralized by the addition of 26.3 g 35% NaOH with stirring at room temperature. The quaternary monomer is then introduced and 150 g purified water and 2 g ammonium persulfate are added. The mixture is stirred, nitrogen is bubbled in and it is heated at 72°C for 24 hours. A cloudy solution is obtained. This concentrated solution precipitates in water, but the precipitate is recovered and purified by precipitation of the synthesis solution in 5 l ethanol. The precipitate is dried to constant weight in the furnace. The yield obtained is 85%.

The polymer obtained dissolves directly at a concentration of 1% by weight in the detergent base from Example 1. Above 4% by weight in this detergent base, NaCl must be added to maintain the solubilization.

PREPARATION EXAMPLE 4

*Synthesis of the copolymer of the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid and trimethylammonio propylmethacrylamide chloride (50/50 mole %).*

A 49.15% aqueous solution of dry extract of 2-acrylamido-2-methylpropane sulfonic acid sodium salt is made by neutralization of the acid with a stoichiometric quantity of NaOH.

Into a reactor identical to that in Example 1 are introduced 103.68 g of the said aqueous solution then 93.43 g of a 52.5% aqueous solution of dry extract of trimethylammonio propyl-methacrylamide chloride. 300 g purified water and 2 g ammonium persulfate are then added. The same conditions are then used as those used in Example 3. The yield obtained is 88%.

The polymer thus obtained is insoluble in water at a concentration of 1% and is solubilized at the same concentration in the presence of at least 3.62% NaCl. It dissolves directly at the same concentration in the detergent base from Example 1. Above 5.5% by weight, an electrolyte must be added to maintain its dissolution.

Example A: Shampoo

| | |
|---|---|
| Sodium lauryl ether sulfate with 22 moles ethylene oxide sold by the ALBRIGHT & WILSON company under the name EMPICOL ESB B/FL | 24 g MA |
| Cocoylbetaine, 32% aqueous solution | 8 g MA |
| Polymer from Example 1 | 1 g MA |
| NaCl | 2 g |

Copolymer of dimethyldiallylammonium chloride/
acrylamide 50/50 in 8% aqueous solution . . . . . . . . . . . . . . . . . . . . . . . . . . . 1 g MA
Preservatives, perfumes
Water.................................qsp . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 100 g

The pH is adjusted to 7 with HCL.

This shampoo has a mild, smooth foam and imparts good discipline and good hold to the hair.

Example B: Lotion to be rinsed off

Trimethylethylammonium methacrylate chloride/
acrylamide (42/58) in 50% dispersion in an oil vehicle . . . . . . . . . . . . . . . . . . . 0.3 g MA
Polymer from Example 1 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 2 g MA
NaCl . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 3 g
Perfumes, colorants, sequestrants
Water..........................qsp . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 100 g

This lotion is easily applied to the hair. After rinsing, the hair is easy to disentangle and style.

Example C: After-shampoo

Cetyltrimethylammonium chloride in 29% aqueous
solution sold by LONZA under the name BURQUAT CT29 . . . . . . . . . . . . . . . . . 1 g MA
Behenyltrimethyl ammonium chloride (80%) in a
water/isopropanol mixture (15/81) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 2 g MA
Hydroxyethylcellulose cross-linked with
epichlorohydrin quaternized with trimethylamine . . . . . . . . . . . . . . . . . . . . . . . 0.5 g MA
Mixture of cetylstearyl alcohol and cetylstearyl
oxyethylene with 33 moles ethylene oxide (88/20) . . . . . . . . . . . . . . . . . . . . . . . . . . 2 g
Xanthan gum . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 0.5 g
NaCl . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 3 g
Polymer from Example 1 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 2 g
Water...........................qsp. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 100 g

The pH is adjusted to 7 with NaOH.

This after-shampoo, after rinsing, brings hold and softness to the hair.

## CLAIMS

1. Compositions for the treatment of keratinic materials characterized by the fact that it contains in a cosmetically and/or dermatologically acceptable aqueous medium at least:

a) one polyampholyte polymer constituted of at least one ethylenically unsaturated monomer containing in the chain or laterally to the chain equimolar or essentially equimolar quantities of negative charges and positive charges, the said polymer being insoluble in water at a concentration higher than or equal to 1% by weight at 20°C;

b) one cationic polymer in which the cationic charge density is less than or equal to 4 meq/g.

2. Composition in accordance with claim 1, characterized by the fact that the ampholyte polymer is chosen from among the polymers corresponding to the following formula:

$$-(\underset{\substack{|\\ D^{(-)},\ X^{(+)}}}{A}-)_{x_1}-(B-)_y-(\underset{\substack{|\\ E^{(+)},\ Y^{(-)}}}{C}-)_{x_2}- \qquad (I)$$

in which:

A designates a group resulting from the copolymerization of an ethylenically unsaturated monomer bearing a group $D^{(-)}$

$D^{(-)}$ designates an anionic group chosen from the group constituted by:

(i) $-COO^{\ominus}$

(ii) $-SO_3^{\ominus}$

(iii) $-PO_3^{2\ominus}$

(iv) $-HPO_3^{\ominus}$

$X^{(+)}$ designates a cation arising from the neutralization of the D groups by an inorganic or organic base;

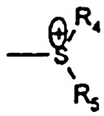
B designates a group resulting from the copolymerization of at least one ethylenically unsaturated hydrophilic or hydrophobic monomer;

C designates a group resulting from the copolymerization of at least one ethylenically unsaturated monomer bearing a group $E^{(+)}$;

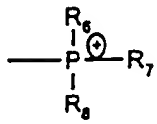
$E^{(+)}$ designates a cationic group chosen from the group constituted by:

(i)
$$-\overset{\overset{\large R_1}{|}}{\underset{\underset{\large R_3}{|}}{N^{\oplus}}}-R_2$$

in which $R_1$, $R_2$ and $R_3$, which are identical or different, designate hydrogen, a linear, branched or cyclic (cycloaliphatic or aromatic) $C_1$-$C_{22}$ alkyl group;

(ii) 

in which $R_4$ and $R_5$, which are identical or different, designate an aliphatic, cycloaliphatic or aromatic group;

(iii) 

where $R_6$, $R_7$, and $R_8$, which are identical or different, designate an aliphatic, cycloaliphatic or aromatic group;

$Y^{(-)}$ designates an anion resulting from the neutralization of the E groups by an inorganic or organic acid or from the quaternization of the E groups;

$x_1$, $x_2$ and y respectively designate the percentages in moles of group A, of group B and of group C, $x_1$ and $x_2$ being identical or essentially identical so that the global charge of the polymer is approximately 0 for a pH close to 7.

3. Composition according to claim 2, characterized by the fact that in the formula (I), the sum $x_1 + x_2$ is higher than or equal to 40 mole% and lower than or equal to 60 mole%.

4. Composition according to claim 2 or 3, characterized by the fact that in the formula (I):

$D^{(-)}$ designates carboxylate and $\underset{\displaystyle D^{(-)}}{\overset{\text{-A-}}{|}}$ is chosen from the group constituted by the salts of linear, branched or cyclic carboxylic acids, the salts of linear, branched or cyclic dicarboxylic acids and their monoesters and monoamides.

5. Composition according to claim 2 or 3, characterized by the fact that in the formula (I):

$D^{(-)}$ designates sulfonate and $\underset{\displaystyle D^{(-)}}{\overset{\text{-A-}}{|}}$ is chosen from the group constituted by the salts of acrylamido-2-methyl-2-propane sulfonic acid, vinylsulfonic acid, and styrenesulfonic acid and the salts of 2-sulfoethyl methacrylate.

6.Composition according to claim 2 or 3, characterized by the fact that $D^{(-)}$ designates phosphonate and $\underset{\displaystyle D^{(-)}}{\overset{\text{-A-}}{|}}$ designates a salt of vinylphosphonic acid.

7. Composition according to any one of the claims 2 to 6, characterized by the fact that the group -B- is constituted by at least one monomer chosen from among the linear, branched or cyclic $C_1$-$C_{24}$ vinyl esters, olefins, styrene and its substituted derivatives; the linear, branched or cyclic $C_1$-$C_{24}$ esters or amides of (meth)acrylic acid and possibly by at least one monomer chosen from the group constituted by the silicone macromers having a terminal vinyl function, vinyl, allyl or (meth)acrylic monomers bearing fluoro or perfluoro groups.

8. Composition according to any one of the claims 2 to 7, characterized by the fact that the monomer -C- is chosen from among the (meth)acrylic, vinyl, allylic or diallylic monomers bearing a tertiary amine
|
$E^{(+)}$
E quaternized by an alkyl halide or a dialkyl sulfate.

9. Composition according to any one of the claims 2 to 8, characterized by the fact that the polymer of formula (I) is chosen from among the group constituted by the sodium styrene sulfonate/trimethylammonio propyl (meth)acrylamide chloride copolymers and the sodium styrene sulfonate/trimethylammonio ethyl methacrylate copolymers.

10. Composition according to claim 1, characterized by the fact that the polyampholyte polymer corresponds to the following formula:

$$CH_2=\underset{R_9}{\underset{|}{C}}-(\underset{O}{\underset{||}{C}}-)_p-(F-)_q-R_{10}-\overset{R_{11}}{\overset{|}{\underset{R_{12}}{\underset{|}{N^{+}}}}}-R_{13}-Z \qquad (II)$$

in which

$R_9$, $R_{11}$ and $R_{12}$, which are identical or different, designate a hydrogen or a linear or branched $(C_1$-$C_4)$-alkyl;

Z designates $COO^{(-)}$, $SO_3^{(-)}$ or $HPO_3^{(-)}$;

F designates NH or O or with the group $R_{10}$ forms an aromatic or non-aromatic $C_5$-$C_7$ ring or heterocycle;

$R_{10}$ and $R_{13}$, independently of each other, designate a divalent hydrocarbon group, in particular a $-(CH_2)_n-$ group with n being a whole number between 1 and 4;

$R_{10}$ can form with $R_{11}$ and $R_{12}$ a $C_5$-$C_7$ heterocycle;

p is 0 or 1 and q is 0 or 1.

11. Composition according to claim 10, characterized by the fact that the polymer of formula (II) is chosen from the group constituted by:

poly 1-vinyl-2-(3-sulfopropyl) imidazolium hydroxide
poly 1-vinyl-3-(3-sulfopropyl) imidazolium hydroxide;
poly 1-vinyl-3-(4-sulfobutyl) imidazolium hydroxide;
poly 1-vinyl-2-methyl-3-(4-sulfopropyl) imidazolium hydroxide;
poly 2-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly 2-methyl-5-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;

poly 2-methyl-5-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly 4-vinyl-1-(3-sulfopropyl) pyridinium hydroxide;
poly dimethyl-(2-methacryloxyethyl)-3-sulfopropyl) ammonium hydroxide;
poly diethyl-(2-methacryloxyethoxy-2-ethyl)-(3-sulfopropyl) ammonium hydroxide;
poly 4-vinyl-4-(sulfobutyl) pyridinium hydroxide;
poly N-(3-sulfopropyl)-N-methacrylamidopropyl-N,N-dimethylammonium betaine

12. Composition according to any one of the claims 1 to 11, characterized by the fact that the polyampholyte polymer is present in concentrations of from 0.01 to 20% by weight, and preferably from 0.1 to 10% by weight relative to the total weight of the composition.

13. Composition according to any one of the claims 1 to 12, characterized by the fact that the cationic polymer has an average molecular weight of at least 5000 and more preferably at least 10,000.

14. Composition according to claim 13, characterized by the fact that the average molecular weight of the cationic polymer varies between 10,000 and 10,000,000.

15. Composition according to any one of the claims 1 to 14, characterized by the fact that the cationic charge density of the cationic polymer varies between 0.9 and 4 meq/g, preferably from 1.1 to 3 meq/g.

16. Composition according to any one of the claims 1 to 15, characterized by the fact that the cationic polymer is chosen from the group constituted by:

a) copolymers of vinyl monomers having primary, secondary, or tertiary amine or quaternary ammonium functions;
b) cationic polysaccharides derived from starch or cellulose derivatives;
c) cationic polymers derived from guar gum;
d) quaternary cellulose ethers, copolymers of etherified cellulose and starch.

17. Composition in accordance with claim 16, characterized by the fact that the cationic polysaccharides of paragraph b) are chosen from among the polymers of formula:

$$\mathrm{H-O-(-R-\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\overset{|}{\underset{|}{N^{+}}}}}-R^3G^-)}$$

where:

H is an anhydroglucose residue such as starch or a cellulosic residue of anhydroglucose;

R is an alkylene, oxyalkylene, polyoxyalkylene or a hydroxyalkylene or their mixtures;

$R^1$, $R^2$ and $R^3$, which are identical or different, designate an alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl group, each group containing up to 18 carbon atoms, and the total number of carbon atoms per cationic unit being preferably less than or equal to 20;

$G^-$ is an anion resulting from the quaternization of the amine $NR^1R^2R^3$.

18. Composition according to any one of the claims 1 to 17, characterized by the fact that the cationic polymer is present in proportions of from 0.01 to 5% by weight and preferably from 0.1 to 3% by weight relative to the total weight of the composition.

19. Composition according to any one of the claims 1 to 18, characterized by the fact that it contains at least one inorganic or organic electrolyte.

20. Composition according to claim 19, characterized by the fact that the electrolyte is present in concentrations of from 0.1 to 30% by weight and preferably from 1 to 10% by weight.

21. Composition according to any one of the claims 1 to 20, characterized by the fact that the pH is adjusted to between 3 and 11.

22. Composition according to any one of the claims 1 to 17, characterized by the fact that it also contains a detergent base constituted of at least one surfactant or a mixture of surfactants chosen from the group of anionic, cationic, non-ionic, amphoteric or zwitterionic surfactants.

23. Composition according claim 22, characterized by the fact that the detergent base represents 4 to 30% by weight of the total weight of the composition.

24. Composition according to any one of the claims 1 to 23, characterized by the fact that the cosmetically or dermatologically acceptable medium is constituted of water or a mixture of water and lower alcohol.

25. Composition according to any one of the claims 1 to 24, characterized by the fact that it also contains adjuvants chosen from the group constituted of the perfumes, preservatives, sequestrants, thickeners, softeners, foam modifiers, colorants, pearlizing agents, hydrating agents, anti-dandruff agents, antiseborrheic agents, vitamins and sun screens.

26. Composition according to any one of the claims 1 to 25, characterized by the fact that it is in the form of a more or less thickened liquid, lotion, cream or gel.

27. Composition according to any one of the claims 1 to 26, characterized by the fact that it is a product to be rinsed off for the washing, care and/or styling of the hair.

28. Process for non-therapeutic treatment of the hair, characterized by the fact that a composition according to any one of the claims 1 to 27 is applied directly on to the hair, and that a rinsing with water is effectuated after an eventual period of stay.